

BASIC ELECTROPOLISHING PROCESS RESEARCH AND DEVELOPMENT IN SUPPORT OF IMPROVED RELIABLE PERFORMANCE SRF CAVITIES FOR THE FUTURE ACCELERATORS*

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Abstract

Future accelerators require unprecedented cavity performance, which is strongly influenced by interior surface nano-smoothness. Electropolishing (EP) is the technique of choice to be developed for high-field superconducting radio frequency (SRF) cavities. Electrochemical impedance spectroscopy (EIS) and related techniques point to the electropolishing mechanism of Nb in a sulphuric and hydrofluoric acid electrolyte controlled by a compact surface salt film under F^- diffusion-limited mass transport control. These and other findings are guiding a systematic characterization to form the basis for cavities process optimization.

INTRODUCTION

Electropolishing is a surface finishing process based on anodic dissolution of a metal or alloy in an appropriately chosen electrolyte [1]. It is believed to be an effective technique to treat niobium cavity surfaces for achieving reproducible high performance SRF cavities [2]. Typically, a mixture of hydrofluoric (49%) and sulfuric acid (96 %) of volume ratio of 1 : 9 or 1:10 has been used with a temperature range of 30°C~40°C, and a current density 40~50 mA/cm² with applied voltage of 10~20 volts.

The electropolishing phenomenon is characterized by the elimination of micro-roughness (leveling) and the absence of crystallographic and grain boundary attack (brightening) and results in the production of smooth, bright surfaces [3-4]. Leveling results from the fact that protruding parts of a rough surface dissolve faster than recessed parts; this can be achieved under either ohmic or mass transport control [5]. Brightening can only occur under mass transport control, which suppresses crystallographic etching [3, 5-7]. There are three types of mass transport limiting species: the cations of dissolving metal (M^{n+}) in the anodic salt film, the electrolyte anions (A^{m-}), and water molecules in the diffusion layer between anode and bulk solution [5].

In this study, the rotating disk electrode (RDE) technique and electrochemical impedance spectroscopy were used to understand the mechanism which governs Nb electropolishing. The electrochemical impedance of the Nb EP process has been measured as a function of

potential and flow rate. The mechanism of Nb electropolishing is identified.

EXPERIMENTAL STUDIES

For RDE experiments, a high purity polycrystalline Nb disc electrode sample was inserted in a Teflon holder with a reactive surface area of 0.19 cm². The Nb discs were mechanically polished up to 4000 grit emery paper, ultrasonically rinsed with isopropanol and distilled water and air dried. A high purity Al wire was used as the counter electrode. The Gamry RDE710 rotating disc electrode setup was used for the experiments. For impedance measurements, a high purity polycrystalline Nb plate imbedded into a Teflon holder with a reactive surface area 4.84 cm² was used as the working electrode. The counter electrode was a high purity Al plate with a surface area 9.68 cm². The reference electrode was a saturated mercury/mercurous sulphate electrode (MSE). The electrolytes were prepared from 49% hydrofluoric and 96% sulphuric acid.

The polarization curves were conducted stepwise (step size=0.1 volts, dwell time=0.25 second) over the potential range from 0 to 22 volts. The potential between the Nb electrode and the reference electrode was recorded using a Keighley 6517A electrometer. The addition of the reference electrode allows monitoring the potentials on the cathode and anode independently. The current was recorded with a Keighley 2000 multi-meter. The data acquisition system was supported by a customized LabView program. Prior to the polarization measurements, the electrodes were immersed in the electrolyte in an open circuit condition for 3 to 5 minutes.

Impedance measurements were performed using a potentiostat (series G300, Gamry Instruments) controlled with a commercial software package (Gamry Instrument Framework). Impedance measurements were performed at constant potential after 120 s, the time at which a steady-state current is attained. The amplitude of potential modulation was 10 mV. Starting with 200 kHz, the modulation frequency was swept automatically down to 0.2 Hz.

EXPERIMENTAL RESULTS

Effect of Rotation

Figure 1 shows the anodic polarization curves determined at the different rotation rates at 30°C. All the curves exhibit a well defined and a wide potential range of limiting current density plateau. It suggests the existence of a salt film; the dissolution rate is mass

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transport controlled and involves diffusion of limited species or the migration of metal ions through a Nernst diffusion layer [8]. Figure 2 shows the typical dependence of the limiting current density on the square root of rotation rate [9]. The limiting current density values were determined on the current plateau at a potential of 6V from Fig 1. The variation of the limiting current density shows a linear behaviour with distinct slope. The non-zero intercept may indicate the presence of a parallel non-diffusion-limited electrode mechanism.

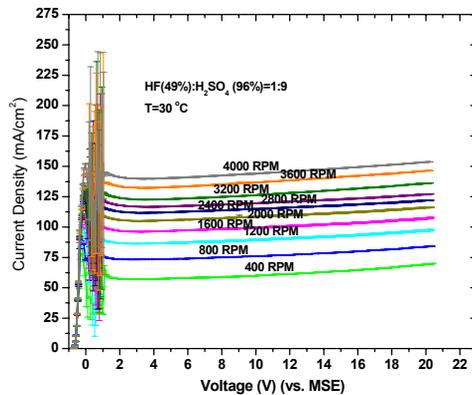


Figure 1: The anode polarization curves of Nb in 1:9 volume ratio HF and H₂SO₄ at 30°C.

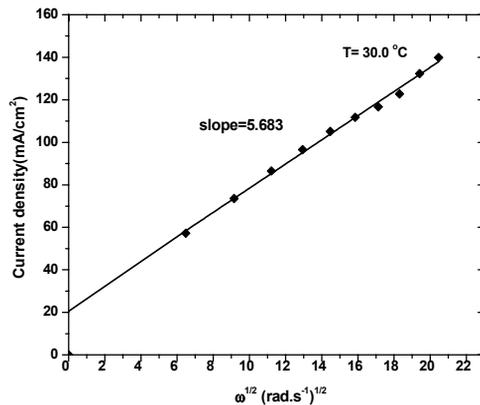


Figure 2: The limiting current density plotted as a function of the square root of rotation rate at a potential 6V (vs. MSE) from Figure 1. Effect of different HF volume concentration.

A series of polarization curves were measured in freshly prepared electrolytes of hydrofluoric and sulphuric as a function of HF to H₂SO₄ volume ratio. The corresponding molar concentration decreases for HF and H₂O from the classical 2.8 mol/L and 6.9 mol/L (HF/H₂SO₄ volume ratio = 1:9) to 0.56 mol/L and 4.65 mol/L (HF/H₂SO₄ volume ratio = 0.02:9.8), respectively, and increases for H₂SO₄ from 16.22 mol/L to 17.66 mol/L. All anode polarization curves exhibit a

limiting current plateau. The anode plateau current density fell linearly with the decreasing HF/H₂SO₄ volume ratio, as shown in Figure 3. This suggests that the polishing rate is directly related to the HF concentration, which is consistent with F⁻ being the diffusion-limited species. The current density changes by a factor of 5 for a factor of 5 change of HF volume content.

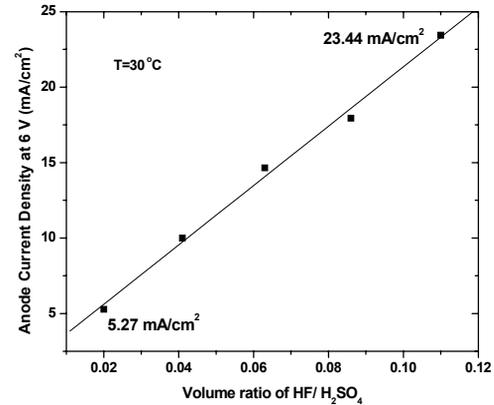


Figure 3: The anode plateau current density decreases with decreasing HF volume ratio.

Electrochemical Impedance Spectroscopy

EIS measurements were made as a function of applied potential under static flow condition. The impedance response was measured as a function of voltage from 2 to 7.8 volt relative to the MSE. Impedance experiments also have been conducted during electrolyte agitation with a magnetic bar directly in the electrochemical cell. The flow rate near the anode surface was estimated to be 4~5 cm/sec. Figure 4 shows a schematic Nyquist plot and equivalent circuit corresponding to the high frequency part of the impedance diagram, where R_s is the solution resistance, R_p is the polarization resistance given by the diameter of circle and C_{dl} is the effective double layer capacitance C_{dl} , determined from the angular frequency at the top of the semicircle and R_p from the relation $\omega_{max} = 1/R_p C_{dl}$.

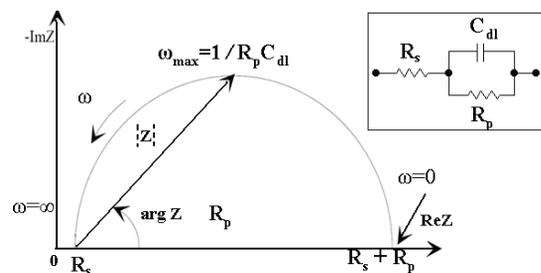


Figure 4: Schematic Nyquist plot and equivalent circuit corresponding to the high-frequency part of the impedance diagram.

Figures 5 and 6 are the results for $T = 9.0 \pm 0.2^\circ\text{C}$ for static and flowing conditions at different applied potential. The anode potential displayed in Figures 5 and 6 is ohmic (IR) corrected; the IR drop is determined from

impedance measurements. Our high frequency impedance data is consistent with a compact salt film model. To summarize; we find that solution resistance, R_s , remains constant at different potentials and flow rates, which rules out application of the porous salt film model [10]. Polarization resistance, R_p , increases with applied potential, while the double layer capacitance decreases. These results are consistent with the compact salt film model only. Static versus agitated electrolyte results further support the compact salt film model [7].

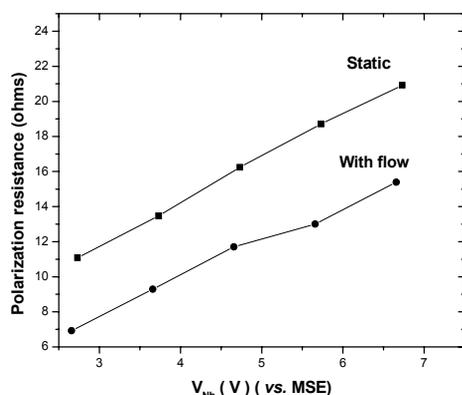


Figure 5: Polarization resistance (R_p) obtained from the high frequency impedance response as a function of different potential and flow rate for Nb EP at 9.0 ± 0.2 °C.

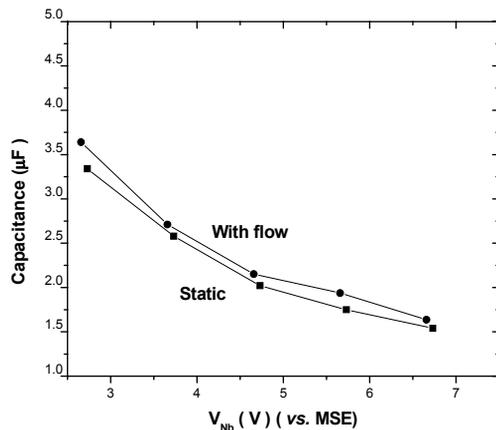


Figure 6: Effective double layer capacitance (C_{dl}) obtained from the high frequency loop as a function of applied potential and flow for Nb EP at 9.0 ± 0.2 °C.

DISCUSSIONS

Results obtained in this study support that the high-rate dissolution of niobium in an electrolyte of 49% hydrofluoric and 96% sulphuric acid is mass-transport controlled with a compact salt film mechanism involved. Previous studies suggest that the mass transport of SO_3^{2-} anions is not responsible for the limiting current [11]. In the presence of HF, a dielectric Nb_2O_5 film tends to be

transformed into soluble fluoride or oxifluoride [2]. As reported, with an additional one proportion of water, decreasing removal rate as compared with the 1:9 mixture was found, and the limiting current was even less or not at all affected by stirring [12]. In addition, the results depicted in Figure 3 indicate that increasing HF content, contrary to the addition of water, favors high niobium dissolution rate. This suggests that the diffusion-limited access of the F^- anion to the salt film limits the dissolution reaction rate.

CONCLUSION

The present data show that electropolishing of niobium in hydrofluoric and sulphuric acid electrolyte strongly depends on HF/ H_2SO_4 volume ratio. High frequency impedance data provide strong evidence for the presence of a compact salt film (Nb_2O_5) in the current-limited plateau region. The available data suggests that the diffusion-limited access of the F^- anion to the salt film surface limits the local reaction rate. Process parameters, such as electrolyte temperature, acid concentrations, viscosity and stirring may affect the F^- anion concentration gradient in the diffusion layer between niobium and bulk electrolyte and therefore have strong effects on the EP process. The knowledge of Nb EP mechanism will be very helpful for optimizing operational parameters and guiding further study for achieving uniform polishing, which will significantly improve the cavity EP production for pursuing a high reproducibility of peak SRF performance.

REFERENCES

- [1] P. A. Jacquet, Nature, 135, 1076 (1935) p, 4,
- [2] F. Eozénou, A. Aspart, C. Antoine and B. Maliki. CARE Report 06-10-SRF. EU contract number RII3-CT-2003-506395 (2006).
- [3] R. Sautebin and D. Landolt, Electrochimica Acta., 129(1982), p. 946.
- [4] R.Sautebin, H. Froidevaux and D. Landolt, J. Electrochem. Soc. 127 (1982), p. 1096.
- [5] D. Landolt, Electrochimica Acta., 32 (1) (1987), p1
- [6] H. Abrams and C.L. Mantell, - Electrochem. Tech. 5(1995), p. 287.
- [7] M. Matlosz, S. Magaino and D. Landolt, J. Electrochem. Soc. 141 (2) (1994), p 410.
- [8] R.D. Grimm, D.Landolt, Corros. Sci. 36(1994), p. 1847.
- [9] V. G. Levich, *Physicochemical Hydrodynamics*, Prentice-Hall New York, 1962.
- [10] H. Tian, Sean G. Corcoran, Charles E. Reece, and Michael J. Kelley, J. of Elec. Soci., 155 (9) 2008, D563-D568.
- [11] I. Sieber, H.Hildebrand, A. Friedrich and P.Schmuki, Electrochem. Comm. 7, (2005), pp. 97.
- [12] H. Shou, Internal report DAPNIA (2003).